Chem 30A Fall 2005
FINAL
(180 Min)
Wed Dec 14th

***DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO***

ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED

INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM – DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU

<table>
<thead>
<tr>
<th>Q1</th>
<th>26 / 26</th>
<th>Q5</th>
<th>2ϕ / 20</th>
<th>Q9</th>
<th>15 / 15</th>
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<tbody>
<tr>
<td>Q2</td>
<td>21 / 21</td>
<td>Q6</td>
<td>31 / 31</td>
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<td>Q3</td>
<td>2ϕ / 20</td>
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<td>32 / 32</td>
<td>Total</td>
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<td>Q4</td>
<td>35 / 35</td>
<td>Q8</td>
<td>3ϕ / 30</td>
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"Organic chemistry just now is enough to drive one mad. It gives me the impression of a primeval forest full of the most remarkable things, a monstrous and boundless thicket, with no way of escape, into which one may well dread to enter." – Friedrich Wöhler (1835)
Q1. (a) Using **LINE FORMULAE** draw the six other **ACHIRAL CONSTITUTIONAL** isomers (B–G) of heptane (A). (2 pt each)  
(b) Name each isomer using **SYSTEMATIC** naming rules. (1 pt each)

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<table>
<thead>
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<tbody>
<tr>
<td>A</td>
<td>heptane</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
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<tr>
<td>C</td>
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<tr>
<td>D</td>
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<tr>
<td>E</td>
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<tr>
<td>F</td>
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<tr>
<td>G</td>
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</table>

Name  

- **B**: 3-ethyl pentane 
- **C**: 2-methyl hexane 
- **D**: 3,3-dimethyl pentane 
- **E**: 2,2-dimethyl pentane 
- **F**: 2,4-dimethyl pentane 
- **G**: 2,2,3-trimethyl butane 

(c) Using **LINE FORMULAE** (and wedges and dashes as necessary) draw the (R)-enantiomers of the two **CHIRAL CONSTITUTIONAL** isomers (H and I) of heptane (A) (3 points each).  
(d) Name each isomer using **SYSTEMATIC** naming rules. (1 pt each)

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<table>
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<tbody>
<tr>
<td>H</td>
<td></td>
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<tr>
<td>I</td>
<td></td>
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</tbody>
</table>

Name  

- **H**: 3-methyl hexane 
- **I**: 2,3-dimethyl pentane
Q2 There are SEVEN different isomers with the formula C₆H₁₂ (J–P) that contain a 4-membered ring, i.e., a cyclobutane ring. Based upon the following statements, draw the appropriate structures (using line formulae with wedges and dashes as necessary) in the boxes below. (3 points each)

(i) J and K are enantiomers of one another

(ii) L and M are diastereoisomers of one another and both are ACHIRAL

(iii) N contains two chiral centers, but is ACHIRAL; it is a diastereoisomer of both J and K

(iv) The monobromination (Br₂/hv) of O gives predominantly a single ACHIRAL compound whereas the monobromination (Br₂/hv) of P results in a mixture of three isomeric compounds, some of which are chiral
Q3. Propose a reasonable mechanism that accounts for the transformation of compound A into compound B shown below – (show all intermediates, all appropriate lone pairs, formal charges, significant resonance forms, and curly arrows). Explain each step with a few words. (20 points)
Q4. When propyne (A) undergoes an oxymercuration reaction \( \text{(Hg(OAc)}_2/\text{H}_2\text{O}/\text{H}_2\text{SO}_4) \) as shown below, the product of the reaction is acetone (C). An intermediate in the reaction is enol B.

(a) Propose a reasonable mechanism that accounts for the acid-catalyzed transformation of enol B into ketone C (i.e., acetone) under the conditions of the oxymercuration reaction – show all intermediates, all appropriate lone pairs, formal charges, significant resonance forms, and curly arrows. Explain each step with a few words. (10 points)

Question 4 is continued on the next page...
(b) If the oxymercuration reaction is performed using methanol (MeOH) rather than water, the product is NOT a ketone, but compound D as shown below. Propose a reasonable mechanism that accounts for the transformation of propyne (A) into compound D – show all intermediates, all appropriate lone pairs, formal charges, and curly arrows. Explain each step with a few words. (20 points)

(c) Suggest a reason why the reaction does not give a ketone as the product when it is performed in methanol rather than water. (5 points)

As can be seen from the above mechanism, the product after one addition is \( \text{CHO} \) rather than an enol, and so tautomerisation to a ketone is not possible.
Q5. An optically active (chiral) compound A (C_{10}H_{16}) reacts with hydrogen in the presence of a platinum (Pt) catalyst to give two diastereoisomeric compounds B and C, each with the formula C_{10}H_{20}. Both B and C are optically inactive (achiral). When A undergoes an ozonolysis reaction (O_3/Me_2S), two compounds are formed; the ketodialdehyde (D) shown below, and compound E (in addition to the byproduct Me_2S=O). Draw the structures of compounds A, B, C, and E, in the boxes at the bottom of this page, including any relevant stereochemistry. (20 pt)

\[
\begin{align*}
C_{10}H_{20} & + C_{10}H_{20} \xrightarrow{\text{Pt}} C_{10}H_{16} \\
\text{(both reagents used in excess)} & \quad \xrightarrow{i) O_3 } D \quad + \quad E \quad \left( \begin{array}{c} \text{CH} \\ \text{SO} \end{array} \right) \\
& \quad \xrightarrow{\text{ii) Me}_2S } \quad \text{IC, so must be } \quad \text{H}_2 \quad \text{H} \\
\end{align*}
\]

Space for working...

3 POSSIBLE CONNECTIONS

1. Racemic mixture of chiral compounds

2. CHIRAL DIASTEREISOMERS

3. ANSWER

A

B

C

E
Q6. (a) The 1-bromo-2,2-dimethylcyclohexane derivative A shown below can exist in two different chair conformations. Complete the skeleton chairs as appropriate in the boxes below. (4 points)

(b) Assign the configuration of the chiral center present in the 1-bromo-2,2-dimethylcyclohexane derivative A shown above. (2 points)

(c) When compound A is heated in methanol (MeOH), alkene B is formed. Propose a reasonable mechanism that accounts for the transformation of A into B - show all intermediates, all appropriate lone pairs, formal charges, significant resonance forms, and curly arrows. Explain each step with a few words and indicate the type of mechanism, i.e., E1, E2, S_N1, or S_N2. (10 points)

CH_3OH removes β proton from position that results in most stable, more substituted alkene

MECHANISM = E1

Question 6 is continued on the next page...
(d) When compound A is heated in methanol (MeOH), not only is alkene B formed, but two diastereoisomeric compounds (C and D) are also produced (each as a pair of enantiomers!) with the molecular formula C₉H₁₈O. Draw the structures of diastereoisomers C and D (using line formulae with wedges and dashes as necessary) in the boxes below. (6 points)

\[ \text{A} \xrightarrow{\text{MeOH, heat}} \text{B} \]

\[ \begin{array}{ccc}
\text{C} & \text{D} \\
\text{C₉H₁₈O} & \text{C₉H₁₈O}
\end{array} \]

Diastereoisomers

(e) When compound A is heated in methanol (MeOH) containing sodium methoxide (NaOMe), a single achiral alkene (E) with the molecular formula C₈H₁₄ is formed. Draw the structure of alkene E in the box below. (3 points)

\[ \text{A} \xrightarrow{\text{MeONa, MeOH, heat}} \text{E} \]

\[ \text{C₈H₁₄} \]

(f) When compound A is reacted with sodium methylthiolate (NaSMe) in acetone, a single chiral compound (F) with the molecular formula C₉H₁₈S is formed. Draw the structure of compound F in the box below. (3 points)

\[ \text{A} \xrightarrow{\text{NaSMe, acetone}} \text{F} \]

\[ \text{C₉H₁₈S} \]

(g) For compounds D, E, and F, indicate what reaction mechanism is responsible for their formation, i.e., E1, E2, Sₐ₁, or Sₐ₂. (3 points).

\[ \begin{array}{ccc}
\text{D} & \text{E} & \text{F} \\
\text{Sₐ₁} & \text{E₂} & \text{Sₐ₂}
\end{array} \]
Q7. Six different cycloalkenes (A–F), each with the molecular formula C₆H₁₀, will yield cis-1,2-dimethylcyclobutane when subjected to catalytic hydrogenation (H₂/Pt catalyst) – as shown below. (Note: in some cases it is the ONLY product, in some cases it is one of two of products).

![Diagram showing the hydrogenation process of cycloalkenes A to F](image)

Furthermore, the results of the ozonolysis reactions (O₃ followed by Me₂S) of these cycloalkenes (A–F), are listed below (in each case the byproduct Me₂S=O is also formed).

<table>
<thead>
<tr>
<th></th>
<th>O₃ (i)</th>
<th>Me₂S (ii)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>A or B</td>
<td>Single Chiral Product</td>
<td>C or D</td>
<td>One Chiral Product and One Achiral Product</td>
</tr>
</tbody>
</table>

(a) Compounds A and B constitute a pair of enantiomers; the absolute configuration of the stereogenic center in compound A is (S) and in B it is (R). Draw these compounds below. (4 points)

![A](image) (S)-Isomer  
![B](image) (R)-Isomer

(b) Compounds C and D also constitute a pair of enantiomers; the absolute configuration of the stereogenic center in compound C is (S) and in D it is (R). Draw these compounds below. (4 points)

![C](image) (S)-Isomer  
![D](image) (R)-Isomer

(c) When compounds A, B, C, and D are hydrogenated, cis-1,2-dimethylcyclobutane is not the only product formed, what two other compounds (G & H) with the formula C₆H₁₂ are also formed (4 points)

![G](image)  
![H](image)
(d) When cycloalkenes E & F are reacted with deuterium gas (D₂) instead of hydrogen gas (H₂), different results are observed.

(i) Cycloalkene E reacts to form a single achiral product (I) – draw these compounds in the appropriate boxes below. (4 points)

(ii) Cycloalkene F reacts to form two diastereomeric compounds (J & K), each of which is achiral – draw these compounds in the appropriate boxes below (note – the labels J & K are arbitrary). (6 points)

(e) No matter which of the six cycloalkenes (A–F) are reacted with hydrogen bromide (HBr), the same two diastereoisomeric compounds (L and M) are formed (each as a pair of enantiomers!) with the molecular formula C₆H₁₁Br. (4 points)

(f) When L undergoes an E1 elimination reaction, three isomeric alkenes can, in theory, be formed. The tetrasubstituted alkene P is the major product, a minor amount of the trisubstituted alkene O is formed, and only trace amounts of the disubstituted alkene N is observed (6 points)
Q8. For each of the reactions shown below draw the MAJOR PRODUCT (paying particular attention to any appropriate stereochemical relationships) in the boxes provided. Note: for two-step reactions, just give the final product, DO NOT draw intermediates. (30 points)

(a)

(b)

(c)

(d)

(e)

Question 8 is continued on the next page...
Q9. Propose a short sequence of reactions (you can't do it in one-step!) that converts 2,3-dimethyl-but-2-ene (A) into 2,3-butadione (B) as depicted below. Show all intermediate compounds, and the reagents necessary for each transformation. DO NOT SHOW MECHANISMS! (15 points)

\[ A \xrightarrow{\text{electrophilic addition of } \text{Br}_2/\text{CCl}_4} \text{Br}_2/\text{CCl}_4 \nrightarrow \xrightarrow{\text{NaOEt/ EtOH}} \text{Me}_2\text{S} \]

\[ \text{double ozonolysis} \]

\[ \text{double } \text{E2 elimination} \]